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Geochemical features and sources of hydrocarbons and fatty acids in soils from the McMurdo Dry Valleys in the Antarctic

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Abstract

We studied the geochemical features and compound-specific (CS)-$\delta^{13}C$ of hydrocarbons and fatty acids in soil samples from the McMurdo Dry Valleys in the Antarctic to elucidate their source organisms and characteristics of their environments. Total organic carbon contents in soil samples were extremely low reflecting extremely harsh environments for organisms. Normal-alkanes ranging in carbon chain length from *n*-C_{14} to *n*-C_{38} with the predominance of odd-carbon numbers were found, together with *n*-alkenes (*n*-$C_{23:1}$ to *n*-$C_{27:1}$). Normal-alkanoic acids ranging in carbon chain length from *n*-C_{10} to *n*-C_{30} with the predominance of even-carbon numbers were detected in the samples, along with small amounts of branched (*iso* and *anteiso*) and *n*-alkenoic acids. CS-$\delta^{13}C$ values of long-chain *n*-alkanes (*n*-C_{20} to *n*-C_{29}) ranged from −30.4 to −26.6‰. CS-$\delta^{13}C$ values of *n*-alkanoic acids with short-chain carbon numbers (*n*-C_{14} to *n*-C_{19}) ranging from −27.7 to −21.7‰ were much higher than those of long-chain carbon numbers (*n*-C_{20} to *n*-C_{30}, −32.5 to −25.3‰). The geochemical features and CS-$\delta^{13}C$ values of long-chain *n*-alkanes and *n*-alkanoic acids revealed that they are originated from lichen and/or vascular plant debris from the pre- and inter-glacial periods in this region, whereas short-chain *n*-alkanoic acids are come from microalgae and cyanobacterial debris. CS-$\delta^{13}C$ values suggest that they are derived from gymnosperms and/or C_4 plants in the cold and dry environments of the pre- and inter-glacial periods of the McMurdo Dry Valleys region.

Keywords: Antarctic soil; Total organic carbon; Total nitrogen; $\delta^{13}C$ of *n*-akanes; $\delta^{13}C$ of *n*-alkanoic acids

1. Introduction

The Antarctic terrestrial environment is extremely harsh for biological activity, and hence vascular plants only occur in the northern part of the Antarctic Peninsula (Greene et al., 1967). Cryptogamic organisms, such as mosses, lichens, algae, cyanobacteria and/or protozoa are however present in most ice-free areas of Antarctica. The McMurdo Dry Valleys in Antarctica are the largest ice-free area extending to 4000 km^2 (e.g., Torii and Yamagata, 1981), and are regarded as one the harshest terrestrial habitats for

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organisms on Earth because of the extremely cold and dry conditions measured there. Although there is a scarcity of conspicuous primary produces in these extreme environments, heterotrophic micro-organisms and invertebrates are present in the valleys (Hopkins et al., 2006; Barrett et al., 2009). Nevertheless, total organic carbon (TOC) contents in soil samples examined from Wright and Taylor Valleys in the McMurdo Dry Valleys are extremely low as a result of the extremely harsh environment for biological activity (Matsumoto et al., 1979; Barrett et al., 2004, 2009; Elberling et al., 2006; Hopkins et al., 2009).

Various kinds of biomarkers, namely, hydrocarbons (*n*-alkanes, *n*-alkenes, triterpanes and steranes), fatty acids (*n*-alkanoic acids, branched acids) and hydroxyl acids (2-, 3- and ω-hydroxy acids) have been reported for soil samples in the McMurdo Dry Valleys (Matsumoto et al., 1981, 1988, 1990a,b; Matsumoto, 2008). Long-chain ($>C_{19}$) *n*-alkanes and *n*-alkenes with the predominance odd-numbers are the major hydrocarbons in most soil samples (Matsumoto et al., 1990a). Also, long-chain *n*-alkanoic acids extending *n*-C_{40} with the predominance of even-carbon numbers are the major fatty acids in soil samples (Matsumoto et al., 1981, 1990b). The occurrence of matured isomers of triterpanes and steranes, the paucity of *n*-alkenoic acids and visual kerogen results suggest strongly that organic components in soil samples are derived from the biological debris containing vascular plant debris in the pre- and inter-glacial periods in Antarctica as well as wind transported cyanobacterial mats from the lakes and ponds in the past, rather than living organisms and from Beacon Supergroup sedimentary rocks (Matsumoto et al., 1990a,b). No one has reported compound-specific (CS)-$\delta^{13}C$ of biomarkers in Antarctica. Here we first report CS-$\delta^{13}C$ of hydrocarbons and fatty acids in soil samples from the McMurdo Dry Valleys in the Antarctic to elucidate their source organisms and the characteristics of their environments.

2. Materials and methods

2.1. Sampling sites and samples

The McMurdo Dry Valleys in southern Victoria Land in Antarctica are dominated by Wright, Taylor and Victoria Valleys (Fig. 1). The valley floors have no ice cover throughout the year, and mainly consist of moraine and fluvioglacial deposits comprising of various sizes of rocks deposited through the Quaternary and Holocene (McKelvey and Webb, 1962). Mean annual air temperatures range from −18 °C in coastal zones to −24 °C in high elevation regions (Aislabie et al., 2006; Barrett et al., 2009). Arid soils underlain by dry permafrost are the most extensive landform of the dry valleys occupying 61% of glacier ice-free surfaces below 1000 m elevation (Barrett et al., 2009).

To obtain more detailed information on lipid biomarkers in soil samples in the McMurdo Dry Valleys, we selected soil samples from our sample collections at Otsuma Women's University taken at the South Fork of Wright Valley on January 11, 1982. These samples we selected as they were anticipated to may contain similar biomarkers to these found in previous studies which would be suitable for the study of the CS-$\delta^{13}C$ of hydrocarbons and fatty acids. Soil samples (0–10 cm) were taken from the flat basin (77°34S, 161°18′E., ca. 250 m above sea level) in the center of the valley depression in the South Fork (Fig. 1, Photo 1) of Wright Valley in the McMurdo Dry Valleys. SF0–SF10 samples were taken in the narrow parts of the valleys within 100 m of each other. Soil samples (fine sand, silt and/or clay) were taken using stainless steel scoop and wrapped with pre-cleaned Teflon sheets to avoid contamination and packed in polyethylene bags. Soil samples were air-transported with dry ice and kept frozen at −30 °C until analyses at the National Institute of Polar Research (Japan), The University of Tokyo and now at Otsuma Women's University.

2.2. Analytical methods

2.2.1. TOC and TN

TOC and total nitrogen (TN) contents were determined by Fisons NCS 2500 automatic elemental analyzer, after treatment with hydrochloric acid to remove carbonate carbon (Matsumoto et al., 2003). The analytical uncertainty was within ±5%.

2.2.2. Hydrocarbon and fatty acid composition

The extraction methods for the organic compounds are given elsewhere (Matsumoto et al., 1979, 2003; Matsumoto and Watanuki, 1992). In short, organic components in soil samples (ca. 40 g) were extracted with ethyl acetate after saponification with 0.5 mol/L potassium hydroxide/methanol-water (80 °C, 2 h). The ethyl acetate extracts were separated by chromatography on a silica gel column (160 mm × 6 mm i.d., 100 mesh, 5% water). Hydrocarbon and fatty acid fractions were obtained by elution with hexane and ethyl acetate, respectively.

A half volume of the fatty acid–sterol fraction was trimethylsilylated (TMS) with 25% *N,O*-bis (trimethyl silyl) acetamide (Matsumoto and Watanuki, 1992).

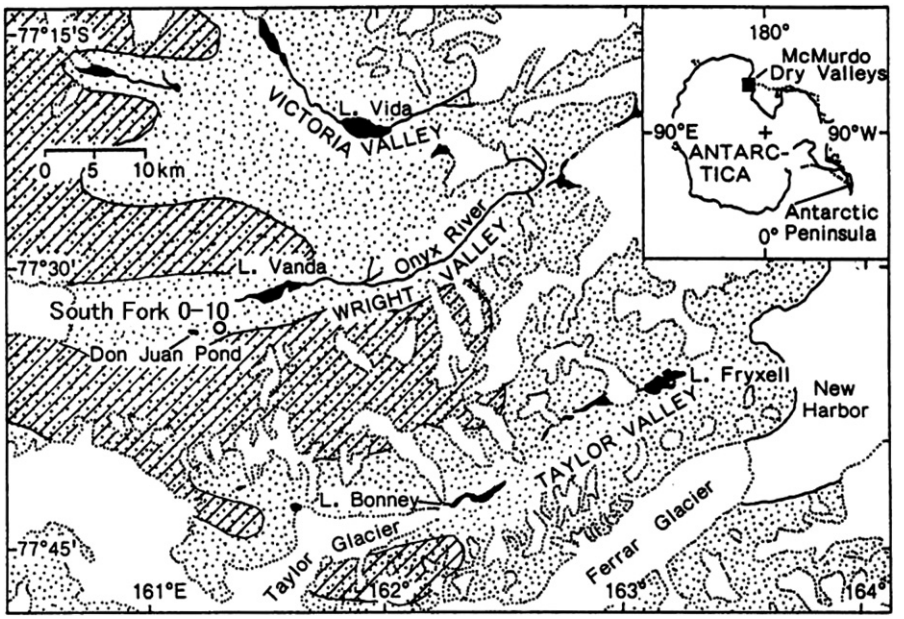

Fig. 1. Sampling locations of soil samples in the South Fork of Wright Valley in the McMurdo Dry Valleys, Antarctica. Slashed areas show outcrops of the Beacon Supergroup of Gondwanaland sediment (McKelvey and Webb, 1962). Dotted areas are ice-free areas. Unmarked areas are glacier ice. Soil samples (0–10 cm) were taken from the flat basin (77°34′S, 161°18′E., ca 250 m a.s.l) of the center of the valley depression in the South Fork on January 11, 1982. SF0–SF10 samples were taken in the narrow parts of the valleys within 100 m of each other.

Hydrocarbons and fatty acid TMS derivatives were analyzed by a JEOL JMS K9 gas chromatograph–mass spectrometer (GC–MS) equipped with a fused-silica capillary column (J&W Scientific DB5, 30 m × 0.25 mm i.d., film thickness 0.1 μm). Splitless mode was employed. Column oven temperature was programmed from 70 to 120 °C at 30 °C/min, and from 120 to 320 °C at 8 °C/min and kept at 320 °C for 3.4 min. The flow rate of the helium carrier gas was 1.2 mL/min. The temperatures of the injector, interface and ion source were maintained at 280, 300 and 250 °C, respectively. Ionization energy, filament current and detector voltage were 70 eV, 200 μA and −1000 V, respectively. The analytical uncertainty was within ±10%.

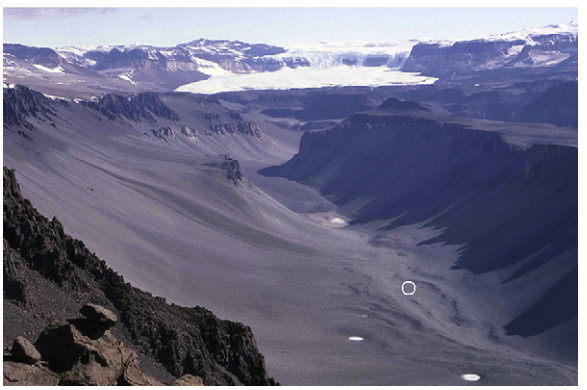

Photo 1. Geomorphological features of sampling sites of soil samples in the South Fork of Wright Valley in the McMurdo Dry Valleys. The photo showing major part of the North Fork viewed from Asgard Range to the westward and top of the photo showing Transantarctic Mountains. Don Juan Pond is located in the center of the depression. Various sizes of rocks are mainly distributed in the surface of the valley floor because of strong winds and past fluvial activity, and sand and silty materials are distributed in depressions of the valley floor. The sampling sites are shown in white circle.

2.2.3. *Compound-specific $\delta^{13}C$ of hydrocarbons and fatty acids*

A portion of the fatty acid fraction was used with batch thermochemolysis in the presence of TMAH (tetramethylammonium hydroxide) to form methyl ester derivatives (similar to McKinney et al., 1996). Briefly, the dried fatty acid fraction was placed in an ampoule and 25% TMAH methanol solution and an internal standard (n-C_{19} alkanoic acid) were added. After the methanol was evaporated under a nitrogen stream to dryness, the ampoule vacuum-encapsulated was set in an electric oven and heated at 300 °C for 30 min. The reacted product was extracted with ethyl acetate.

CS-$\delta^{13}C$ of hydrocarbons and fatty acids was determined using a Thermo Scientific Delta V Advantage interfaced with a Thermo Scientific Trace GC ULTRA via a combustion furnace. Combustion was performed in a microvolume ceramic tube with CuO/NiO/Pt wires at 1000 °C (similar to Hayes et al., 1990). The GC column

used was J&W Scientific HP-5MS (30 m length, 0.25 mm i.d., 0.25 μm film thickness) fused-silica capillary column and the column temperatures were programmed from 60 °C isothermal for 2 min at 6 °C/min to 310 °C and then held isothermal for 20 min. Co-injected *n*-alkanes, whose isotopic compositions were determined independently, were used for the $\delta^{13}C$ determination of *n*-alkanes and *n*-alkanoic acids, respectively. The $\delta^{13}C$ values obtained for *n*-alkanoic acids were corrected for the effects of the additional carbon atom from the TMAH reagent [$N(CH_3)_4OH$, $\delta^{13}C = -37.4‰$] used in their derivatization. Reported carbon isotopic compositions were expressed as conventional *d* notations relative to Vienna Peedee Belemnite (VPDB) and as averaged values based on triplicate injections with standard deviations. The standard deviations of three replicate analyses for compound-specific $\delta^{13}C$ of *n*-alkanes and *n*-alkanoic acids are shown in Figs. 4 and 5, respectively, as error bars.

3. Results and discussion

3.1. TOC and TN

TOC and TN contents in soil samples from the South Fork in Wright Valley in the McMurdo Dry Valleys ranged from 0.0058 to 0.0806% and 0.000 to 0.020%, respectively (Table 1). These values are extremely low and similar to those of previous results (Matsumoto et al., 1979; Barrett et al., 2004, 2009; Elberling et al., 2006; Hopkins et al., 2009). TOC contents reflect extremely harsh environments limiting biological activity. TOC/TN weight ratios in soil samples varied widely ranging from 1.3 to 9.6 (Table 1). The extremely low value of 1.3 may be due to large contribution of inorganic nitrogen such as nitrate in the McMurdo Dry Valleys (Torii and Yamagata, 1981; Wada et al., 1981; Burkins et al., 2000; Elberling et al., 2006; Hopkins et al., 2009).

3.2. Geochemical features of hydrocarbons and fatty acids

A suite of *n*-alkanes ranging in carbon chain length from *n*-C_{15} to *n*-C_{37} was found in the SF0a soil sample from the South Fork of Wright Valley with a predominance of odd-carbon numbers maximizing at *n*-C_{23}, together with alkenes [$C_{23:1}$ (carbon chain length: number of unsaturation)−$C_{27:1}$, Fig. 2]. Major hydrocarbons (>10%) in soil samples were *n*-C_{23}, *n*-C_{25} and/or *n*-C_{27} alkanes as in the case of previous studies (Table 2, Matsumoto et al., 1990a,b). Normal-alkenes were found in the SF0a, SF3 and SF9 samples with a predominance of odd-carbon numbers with relatively small percentages (0.0−14.4%) in total hydrocarbons (Table 2). Long-chain *n*-alkanes are major components of hydrocarbons (76.9−89.2%) in all the samples studied (Table 2). Normal-long (*n*-C_{20} to *n*-C_{38})/short (*n*-C_{15} to *n*-C_{19}) chain-alkane ratios were considerably high ranging from 6.6 to 10.7. Carbon preference indices (CPI_H) for *n*-alkanes were relatively low (2.0−2.6, Table 2) compared with recent sediments.

A series of *n*-alkanoic acids ranging in carbon chain length from *n*-C_{10} to *n*-C_{30} maximizing at *n*-C_{24} were detected in soil sample SF0a from the South Fork in Wright Valley with a predominance of even-carbon numbers, along with *n*-alkenoic ($C_{16:1}$ and $C_{18:1}$) and branched (*iso* and *anteiso*) acids (Fig. 3). The major fatty acids were *n*-C_{12}, *n*-C_{24}, *n*-C_{26} and/or *n*-C_{28} alkanoic acids (Table 3) as in the case of the previous studies, except for *n*-C_{12} alkanoic acid (Matsumoto et al., 1981, 1990b). As the predominance of *n*-C_{12} alkanoic acid in natural environments as well as living organisms is not known, further studies are required for its source materials. Alkenoic acids were very small (0.40−4.2%). Branched acids were found in all the samples, but their percentages were small (1.5−5.3%, Table 3). Long-chain *n*-alkanoic acids are major components of fatty acids (50.5−74.0%) and were present in all the samples studied (Table 3). Normal-long (*n*-C_{20} to *n*-C_{30})/short (*n*-C_{10} to *n*-C_{19}) chain-alkanoic acid ratios were considerably high ranging from 1.2 to 3.1 (Table 3). Carbon preference indices for *n*-alkanoic acids (CPI_F) were relatively low (1.5−2.1) as in the case of previous studies (Matsumoto et al., 1990b).

3.3. Compound-specific $\delta^{13}C$ values of hydrocarbons and fatty acids

CS-$\delta^{13}C$ of *n*-alkanes was determined for two samples (SF0a, SF9), but could not be determined for SF3 and SF8 samples because of too low concentrations.

Table 1
Total organic carbon (TOC) and total nitrogen (TN) contents in soil samples from the McMurdo Dry Valleys, Antarctica.

Sample	Major grain size	Color	TOC/%	TN/%	TOC/TN
South Fork-0a (SFOa)	Fine sand and silt	Glayish olive 5/2	0.0268	0.000	–
South Fork-3 (SF3)	Fine sand and silt	Gray 4/1	0.0058	0.004	1.3
South Fork-8 (SF8)	Fine sand and silt	Olive 5/4	0.0288	0.003	9.6
South Fork-9 (SF9)	Silt and clay	Glayish olive 5/3	0.0806	0.020	4.1

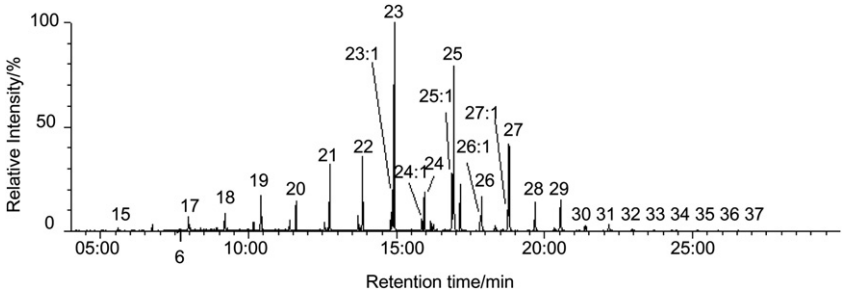

Fig. 2. Mass chromatogram (m/z 57) of hydrocarbon fraction from soil samples (SF3) in the McMurdo Dry Valleys. Arabic figures on the peaks denote carbon chain length of *n*-alkanes. 23:1−27:1 are carbon chain length: number of unsaturation.

The CS-δ^{13}C of *n*-alkanes in soil sample SF0a ranged −30.4 to −27.1‰ with the maximum value at *n*-C_{26} alkane + alkene and minimum value at *n*-C_{28} alkane (Fig. 4), although *n*-C_{23} to *n*-C_{27} alkanes were a mixture of mono-alkenes as shown in Table 2. Similar results for the CS-δ^{13}C of *n*-alkanes were obtained in SF9 sample, except for *n*-C_{17} alkane which has a lower value (−30.7‰). CS-δ^{13}C values of *n*-alkanoic acids in soil sample SF0a have a wide range variation ranging from −31.8 to −23.9‰ with the maximum value at *n*-C_{16} alkanoic acid and the minimum value at *n*-C_{23} alkanoic acid (Fig. 5). CS-δ^{13}C values of short-chain *n*-alkanoic acids (*n*-C_{14} to *n*-C_{18}) were much higher than those of long-chain *n*-alkanoic acids (*n*-C_{20} to *n*-C_{30}). Similar CS-δ^{13}C results of *n*-alkanoic acids were obtained for SF3, SF8 and SF9 soil samples (Fig. 5). The patterns of CS-δ^{13}C values of *n*-alkanes and *n*-alkanoic acids were somewhat different between samples, implying that these compounds comprise a mixture of different organic sources.

3.4. Sources of hydrocarbons and fatty acids

Soil organic matter in the McMurdo Dry Valleys is derived from multiple sources, namely, marine, lacustrine and endolithic sources. Modern distribution patterns of low-elevation soil organic matter in the valleys are strongly influenced by the climatic history of the region, corresponding to the spatial distribution of ancient glacial tills and lacustrine systems, such as ancient lake deposits (legacies) along the valley floor. Also, soils at many higher elevation sites include organic matter derived from autotrophs such as those currently inhabiting nearby cryptoendolithic microbial communities including lichens. This suggests that similar autotrophic activity may be occurring in these soils and that long-term primary productivity in the valley soils contributes to the accumulation of organic matter (Burkins et al., 2000; Hopkins et al., 2006, 2009; Barrett et al., 2009). In addition, another potential source of organic components in soils is vascular plant debris derived from the pre- and inter-glacial periods including the Beacon Supergroup sedimentary rocks in the McMurdo Dry Valleys and adjacent regions (Matsumoto et al., 1990a,b).

Short-chain *n*-alkanes, alkenes and *n*-alkanoic acids are widely distributed in algae and cyanobacteria. Long-chain *n*-alkanes having a predominance of odd-carbon numbers (high CPI_H values) are usually believed to be derived from the waxes of vascular plants, while those having near unity values of odd/even ratios (low CPI_H values) are thought to be derived from bacterial lipids, eroded materials from sedimentary rocks, or petroleum and their products. Long-chain *n*-alkanoic acids with high CPI_F values in environmental samples are derived from vascular plants, whereas those of near unity CPI_F values are originated from eroded materials from sedimentary rocks (e.g., Matsumoto et al., 1990b, 2004).

The hydrocarbon compositions of Antarctic mosses (*Pottia heimii*, *Sarconeurum glaciale*, *Bryum pseudotriquetrum*) are considerably different from those of soil samples (Matsumoto and Kanda, 1985). The δ^{13}C values of organic carbon of mosses (−27 to −25‰, Hopkins et al., 2009) are similar to the CS-δ^{13}C values of *n*-alkanes and *n*-alkanoic acids (Figs. 4 and 5), although no terrestrial moss communities are visibly present in Wright Valleys. Mosses are, thus, unlikely sources of the long-chain compounds in soils. However, long-chain *n*-alkanes (*n*-C_{20} to *n*-C_{36}) and *n*-alkanoic acids (*n*-C_{20} to *n*-C_{32}) have been found in endolithic microbial communities in the Beacon Supergroup sandstone from the Linnaeus Terrace, Mount Fleming and Battleship Promontory in the McMurdo Dry Valleys, together with often long-chain *anteiso*-alkanes (a-C_{20} to a-C_{30}) and *anteiso*-alkanoic acids (a-C_{20} to a-C_{30}, Matsumoto et al., 1992, 2004). Some lichen dominated community does, however, not contain *anteiso*-components. The δ^{13}C values of

Table 2
Hydrocarbon composition found in soil samples from the McMurdo Dry Valleys, Antarctica (%).

Hydrocarbon	SF0a	SF3	SF8	SF9
n-Short				
14	0.00	0.00	0.21	0.11
15	0.25	0.55	0.36	0.20
16	0.59	1.59	0.82	0.61
17	1.36	2.49	2.44	2.63
18	1.68	3.10	2.70	2.28
19	3.40	4.44	4.32	5.88
n-Short/%	7.28	12.17	10.85	11.71
n-Long				
20	2.88	4.18	4.56	4.29
21	6.40	6.04	9.56	7.41
22	7.12	5.68	9.67	7.78
23	20.17	7.70	17.05	14.46
24	3.77	4.52	5.83	3.44
25	16.40	15.35	16.30	11.33
26	3.56	4.88	5.70	4.44
27	9.09	14.83	13.33	14.35
28	3.16	5.02	2.46	2.97
29	3.44	7.25	2.63	4.33
30	0.62	1.10	0.38	0.47
31	0.70	1.68	1.12	1.03
32	0.21	0.43	0.16	0.16
33	0.18	0.38	0.20	0.19
34	0.13	0.23	0.07	0.09
35	0.13	0.24	0.06	0.10
36	0.06	0.15	0.04	0.06
37	0.08	0.15	0.03	0.02
38	0.00	0.05	0.02	0.00
n-Long/%	78.10	79.86	89.17	76.92
n-Alkene				
23:1	3.93	0.34	0.00	3.14
24:1	1.16	1.11	0.00	1.02
25:1	5.69	3.24	0.00	4.20
26:1	1.61	1.52	0.00	0.97
27:1	2.23	1.76	0.00	2.00
n-Alkene/%	14.62	7.97	0.00	11.33
Total/%	100.00	100.00	100.00	100.00
n-Long/*n*-Short	10.73	6.56	8.22	6.57
CPI_H (C_{14}–C_{38})	2.59	1.98	2.07	2.32

endolith-derived organic matter (−31 to −22‰, Hopkins et al., 2009) are similar to those CS-$\delta^{13}C$ values of *n*-alkanes and *n*-alkanoic acids (Figs. 4 and 5). It is therefore most likely that such lichens are important sources of the long-chain *n*-alkanes and *n*-alkanoic acids found in soil samples.

Long-chain *n*-alkanes and *n*-alkanoic acids with small CPI_H and CPI_F values are likely to originate from lichens and/or vascular plants debris in ancient materials, such as biological activity in the pre- and inter-glacial periods. The paucity of *n*-alkenoic acids supports the interpretation that fatty acids are mainly derived from residual organic matter rather than living organisms, because *n*-alkenoic acids are degraded faster than *n*-alkanoic acids (Matsumoto et al., 2004). Although mean residence times of soil organic carbon in the dry valleys were estimated to be 10–123 years (Barrett et al., 2006; Elberling et al., 2006; Hopkins et al., 2009), the occurrence of triterpanes and steranes with various degrees of maturation and coals in soil samples showed, however, that a part of the organic matter present is derived from ancient vascular plant debris (Matsumoto et al., 1990b).

The occurrence of long-chain *n*-alkenes in soil samples is very unusual (Table 2), but they have also been found as the major hydrocarbons in other soil samples from the McMurdo Dry Valleys (Matsumoto et al., 1990a). Long-chain *n*-alkenes with odd-carbon preferences are probably derived from various cyanobacteria and microalgae which lived in the past but not the present (Matsumoto et al., 1990a). Branched (*iso* and *anteiso*) alkanoic acids are widely distributed in bacteria (O'Leary, 1982) including psychrophilic bacteria isolated from cyanobacterial mats in the McMurdo Dry Valleys, Antarctica (Reddy et al., 2000, 2003a,b).

CS-$\delta^{13}C$ values of organic compounds are useful for the study of sources of organic matter in geological and environmental samples. CS-$\delta^{13}C$ values of *n*-alkanes and *n*-alkanoic acids of C_3 plants are much lower than those of C_4 plants. CS-$\delta^{13}C$ values of CAM plants are

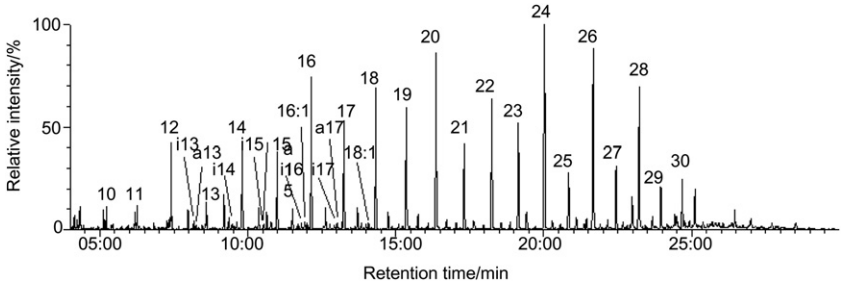

Fig. 3. Mass chromatogram (*m*/*z* 117) of trimethyl silyl derivatives of fatty acid fraction from soil sample (SF3) in the McMurdo Dry Valleys. Arabic figures on the peaks denote carbon chain length of *n*-alkanoic acids. i: *iso*-alkanoic acid. a: *anteiso*-alkanoic acid. 16:1 and 18:1 are carbon chain length: number of unsaturation.

Table 3
Fatty acid composition found in soil samples from the McMurdo Dry Valleys, Antarctica (%).

Fatty acid	SF0a	SF3	SF8	SF9
n-Short				
10	0.91	1.37	0.54	0.94
11	0.98	0.66	0.50	1.10
12	3.48	10.50	1.06	1.86
13	1.08	0.74	0.58	1.34
14	3.28	7.32	1.97	3.51
15	3.13	2.95	1.80	2.94
16	6.11	8.08	4.57	5.68
17	4.33	3.31	4.09	3.87
18	5.67	4.41	4.22	4.53
19	4.87	2.46	4.63	3.75
n-Short/%	33.84	41.80	23.96	29.52
n-Long				
20	7.07	4.23	5.76	5.34
21	3.62	2.86	4.72	3.40
22	5.93	3.96	6.78	6.13
23	5.11	2.77	6.79	5.52
24	10.36	4.46	9.70	9.94
25	3.02	3.24	5.84	3.45
26	10.08	6.26	8.82	9.56
27	3.71	5.22	6.18	5.11
28	8.65	8.59	9.47	10.10
29	2.65	4.21	3.36	2.85
30	3.18	4.73	6.62	3.43
n-Long/%	63.38	50.53	74.04	64.83
Branched				
i12	0.07	0.00	0.15	0.00
i13	0.33	0.19	0.00	0.00
a13	0.16	0.26	0.00	0.21
i14	0.47	0.90	0.30	0.71
i15	0.22	0.36	0.24	0.63
a15	0.67	0.95	0.53	2.73
i16	0.20	0.32	0.16	0.45
i17	0.04	0.10	0.00	0.15
a17	0.15	0.37	0.12	0.37
Branched/%	2.31	3.45	1.50	5.25
Unsaturated				
16:1	0.21	2.58	0.30	0.22
18:1	0.24	1.64	0.21	0.18
Unsaturated/%	0.45	4.22	0.51	0.40
Total/%	100.00	100.00	100.00	100.00
n-Long/*n*-Short	1.87	1.21	3.09	2.20
CPI_F (C_{10}–C_{30})	1.93	2.14	1.45	1.77

in the middle ranges between C_3 and C_4 plants (Collister et al., 1994; Chikaraishi and Naraoka, 2007; Chikaraishi and Oba, 2008). In addition, CS-δ^{13}C values of *n*-alkanes and *n*-alkanoic acids of angiosperms are somewhat lower than those of gymnosperms (Collister et al., 1994; Naraoka, 2004). CS-δ^{13}C values of long-chain *n*-alkanes (−30.4 to −26‰, Fig. 4) in soil samples are similar to those of vascular plants mainly of gymnosperms (−34 to −30‰) rather than angiosperms (−39 to −32‰, Collister et al., 1994; Lockheart et al., 1997; Naraoka, 2004).

CS-δ^{13}C values of long-chain *n*-alkanoic acids (−30.4 to −26‰, Fig. 5) in the South Fork soil samples are consistent again with those of gymnosperms (−33 to −29‰) and much higher than angiosperms (−40 to −34‰, Collister et al., 1994; Naraoka, 2004). In contrast, CS-CS-δ^{13}C values of short-chain (*n*-C_{14} to *n*-C_{18}) *n*-alkanoic acids (−27.7 to −21.7‰, Fig. 5) in the soil samples were considerably higher than those of long-chain ones (Fig. 5). These short-chain *n*-alkanoic acids may be derived from other sources, such as microalgae and cyanobacteria. Indeed, δ^{13}C values of organic carbon in Lake Hoare and Lake Chad mats (−19.9 to −27.7‰, Burkins et al., 2000), cyanobacteria and algae (approximately −10‰, Hopkins et al., 2009) are close to our CS-δ^{13}C of short-chain *n*-alkanoic acids, although generally δ^{13}C values of lipid molecules are generally somewhat lower than those of whole organisms (e.g.,Naraoka, 2004).

It is possible that gymnosperms were the dominant plants in the McMurdo Dry Valley region in the Cretaceous and Cenozoic periods. CS-δ^{13}C values of long-chain *n*-alkanes and *n*-alkanoic acids in the soil samples can be, however, explained by the mixture of C_3 and C_4 plants. Makou et al. (2007) reported that C_3 vegetation predominated during the wet and warm Bølling/Allerød and Preboreal periods, while C_4 plants are more proliferated during cooler and arid periods, such as the glacial and Younger Dryas in Cariaco Basin sediments. In the cold and dry environments of the McMurdo Dry Valleys, it is very likely that C_4 plants contributed to *n*-alkanes and *n*-alkanoic acids found in soil samples in the past. δ^{13}C values of organic carbon in soils from Wright and Taylor Valleys ranged from −27 to −24‰, and from −32 to −28‰, respectively (Hopkins et al., 2009). These δ^{13}C values are similar to those of vascular plants (−37 to −21‰, Deins, 1980; Yoshioka, 2006). This is consistent with ancient vascular plant debris contributing to the McMurdo Dry Valleys soils.

As discussed elsewhere, no atmospheric fallout derived from mid and lower latitudes, and the Beacon Supergroup of Gondwanaland sediments (Barrett and Kyle, 1975; Barrett, 1991) are major sources of long-chain *n*-alkanes and *n*-alkanoic acids in soil samples from the McMurdo Dry Valleys (Matsumoto et al., 1900a,b). Several drilling projects (CIROS, CRP and ANDRILL, etc.) in the McMurdo Sound region have shown paleoclimatic change, tectonic and glacial history of over the last 34 million years along the Victoria Land margin (e.g, Barrett et al., 1989; Thorn, 2001; Prebble et al., 2006; Warny et al., 2009). They showed the occurrence of woody vegetation, including *Nothofagus* and *Libocedrus* with local areas of glass in

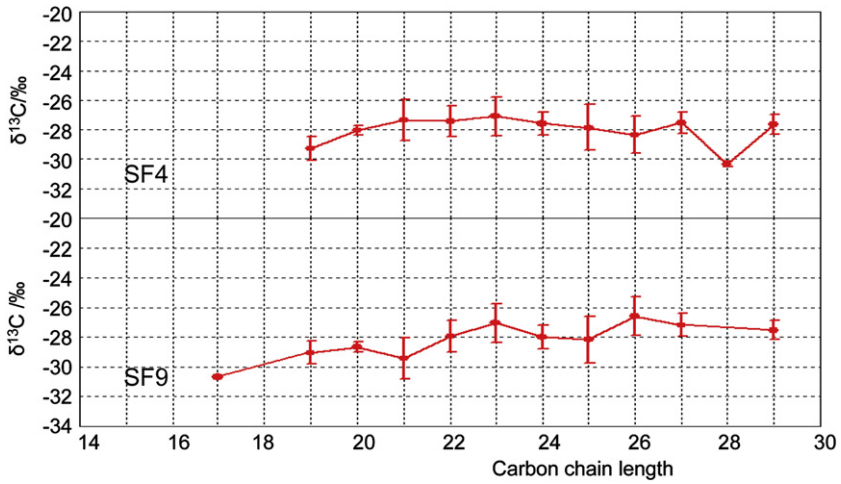

Fig. 4. Compound-specific $\delta^{13}C$ values of *n*-hydrocarbons found in soil samples from the McMurdo Dry Valleys. Normal-C_{23}, *n*-C_{24}, *n*-C_{25}, *n*-C_{26} and *n*-C_{27} hydrocarbons are mixture of *n*-alkanes and *n*-alkenes as shown in Table 2. Error bars show the standard deviation of three replicate analyses.

the most exposed location in Oligocene and Early Miocene (Thorn, 2001; Prebble et al., 2006), tundra environments in the Neogene Sirius Group (Francis et al., 2007), and proliferation of woody plants in the Middle Miocene (Warny et al., 2009). Various organisms including vascular plant debris may be buried and preserved under the ice sheet. In the McMurdo Dry Valleys, glacially eroded materials including vascular

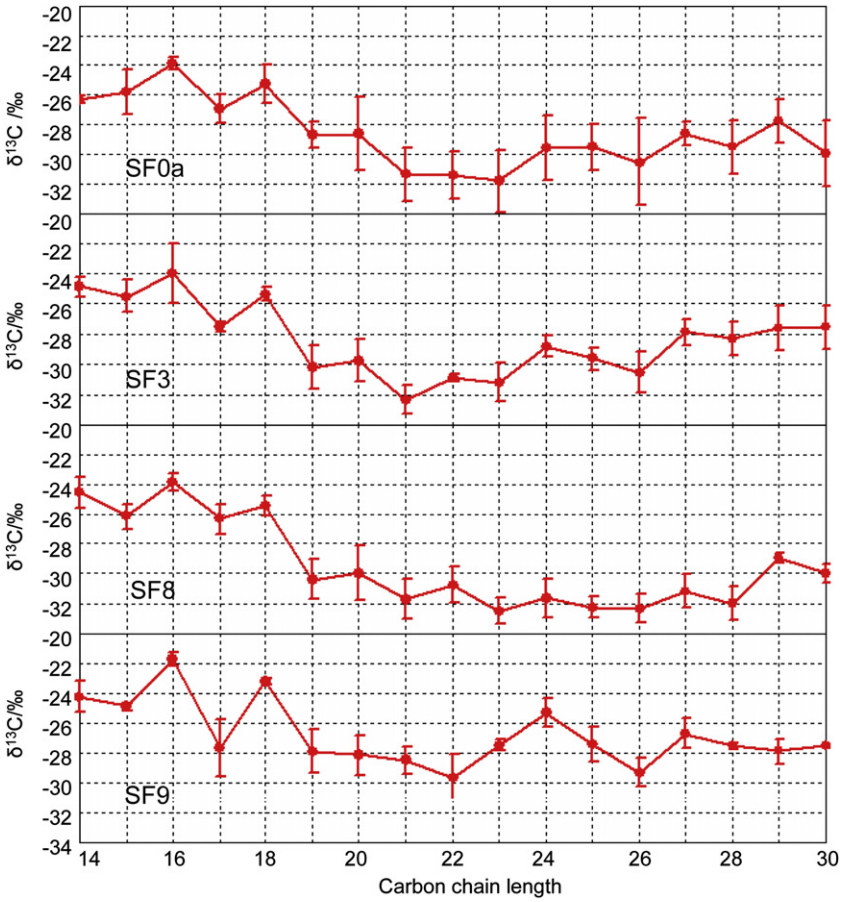

Fig. 5. Compound-specific $\delta^{13}C$ values of *n*-alkanoic acids found in soil samples from the McMurdo Dry Valleys. Error bars show the standard deviation of three replicate analyses.

plant debris are probably distributed in the valley depressions as moraine (Matsumoto et al., 1990a). CS-$\delta^{13}C$ values of *n*-alkanes and *n*-alkanoic acids suggest that they are derived from gymnosperms and/or C_4 plants in the cold and dry environments of the pre- and inter-glacial periods of the McMurdo Dry Valleys and adjacent regions. No data are, however, available on CS-$\delta^{13}C$ of biomarkers of major organisms, such as lichens, cyanobacteria and algae in Antarctica. Further studies on CS-$\delta^{13}C$ of biomarkers including hydrocarbons and fatty acids in these communities will be required to elucidate sources of organic matter in the McMurdo Dry Valleys.

4. Conclusions

Geochemical features and CS-$\delta^{13}C$ of hydrocarbons and fatty acids in soil samples from the McMurdo Dry Valleys of southern Victoria Land, Antarctica were studied to elucidate their source organisms and characteristics of their environments. The results are summarized as follows.

1) TOC and TN contents in soil samples are extremely low reflecting extremely harsh environments for organisms.
2) Normal-alkanes ranging carbon-chain length of *n*-C_{14} to *n*-C_{38} with the predominance of long-chain components with low CPI_H values are found in soil samples, along with *n*-alkenes (*n*-$C_{23:1}$ to *n*-$C_{27:1}$).
3) Normal-alkanoic acids ranging carbon-chain length of *n*-C_{10} to *n*-C_{30} with the predominance of long-chain components with relatively low CPI_F values, together with small amounts of branched (*iso* and *anteiso*) and *n*-alkenoic acids are present.
4) Gechemical features of long-chain *n*-alkanes and *n*-alkanoic acids suggest that they originate from lichens and/or vascular plant debris in the pre- and inter-glacial periods of the McMurdo Dry Valley region, whereas short-chain *n*-alkanoic acids are come from microalgae and cyanobacterial debris in the past.
5) CS-$\delta^{13}C$ values of *n*-alkanes and *n*-alkanoic acids suggest that they are derived from gymnosperms and/or C_4 plants in the cold and dry environments in the pre- and inter-glacial periods of the McMurdo Dry Valleys region.

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References

Aislabie, J.M., Chhour, K.L., Saul, D.J., Miyauchi, S., Ayton, J., Paetzold, R.F., Bulks, M.R., 2006. Dominant bacteria in soils of Marble Point and Wright Valley, Victoria land, Antarctica. Soil Biol. Biochem. 38, 3041−3056.

Barrett, P.J., 1991. The Devonian to Jurassic Beacon supergroup of the transantarctic mountains and correlatives in other parts of Antarctica. In: Tingey, R.J. (Ed.), The Geology of Antarctica. Clarendon Press, Oxford, pp. 120−152.

Barrett, P.J., Hambrey, M.J., Harwood, D.M., Pyne, A.R., Webb, P.-N., 1989. Synthesis. In: Barrett, P.J. (Ed.), Antarctic Cenozoic History from the CIROS-1 Drillhole, McMurdo Sound, vol. 245. DSIR Bull., pp. 241−251.

Barrett, J.E., Virginia, R.A., Wall, D.H., Parsons, A.N., Powers, L.E., Burkins, M.B., 2004. Variation in biogeochemistry and soil biodiversity across spatial scales in a polar desert ecosystem. Ecology 85, 3105−3118.

Barrett, J.E., Virginia, R.A., Parsons, A.N., Wall, D.H., 2006. Soil carbon turnover in the McMurdo Dry Valleys, Antarctica. Soil Biol. Biochem. 38, 3065−3082.

Barrett, J.E., Gooseff, M.N., Takacs-Vesbach, C., 2009. Spatial variation in soil active-layer geochemistry across hydrologic margins in polar desert ecosystems. Hydro. Earth Syst. Sci. 13, 2349−2358.

Barrett, P.J., Kyle, R.A., 1975. The early Permian glacial beds of South Victoria Land and the Darwin Mountains, Antarctica. In: Campbell, K.S.W. (Ed.), Gondowana Geology. Australian National University Press, Canberra, pp. 333−346.

Burkins, M.B., Virginia, R.A., Chamberlain, C.P., Wall, D.H., 2000. Origin and distribution of soil organic matter in Taylor Valley, Antactica. Ecology 81, 2377−2391.

Chikaraishi, Y., Naraoka, H., 2007. $\delta^{13}C$ and δD relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. Org. Geochem. 38, 198−215.

Chikaraishi, Y., Oba, Y., 2008. Compound-specific isotope analysis (CSIA) by gas chromatograph/isotope ratio mass spectrometer (GC/IRMS). Res. Org. Geochem. 23/24, 99−122 (in Japanese with English abstract).

Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific $\delta^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms. Org. Geochem. 21, 619−627.

Deins, P., 1980. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of environmental isotope geochemistry. Elsevier, Amsterdam, pp. 329−406.

Elberling, B., Gregorich, E.G., Hopkins, D.W., Sparrow, A.D., Novis, P., Greenfield, L.G., 2006. Distribution and dynamics of soil organic matter in an Antarctic dry valleys. Soil Biol. Biochem. 38, 3095−3106.

Francis, J.E., Haywood, A.M., Ashworth, A.C., Valdes, P.J., 2007. Tundra environments in the Neogene Sirius Group, Antarctica: evidence from the geological record and coupled atmosphere-vegetation models. J. Geol. Soc. 164, 317−322.

Greene, S.W., Gressitt, J.L., Koob, D., Llano, G.A., Rudolph, E.D., Singer, R., Steere, W.C., Ugolini, F.C., 1967. Terrestrial life of Antarctica. In: Bushnell, V.C. (Ed.), Antarctic Map Folio Ser. Folio 5. Amer. Geophys. Soc., New York, pp. 1−24.

Hayes, J.M., Freeman, K.H., Popp, B.N., Hoham, C.H., 1990. Compound-specific isotope analyses: a novel tool for reconstruction of ancient biogeochemical processes. Org. Geochem. 16, 1115–1128.

Hopkins, D.W., Sparrow, A.D., Novis, P.M., Gregorich, E.G., Elberling, B., Greenfield, L.G., 2006. Controls on the distribution of productivity and organic resources in Antarctic Dry Valley soils. Proc. Royal Soc. B 273, 2687–2695.

Hopkins, D.W., Sparrow, A.D., Gregorich, E.G., Elberling, B., Novis, P., Fraser, F., Scrimgeour, C., Dennis, P.G., Meier-Augenstein, W., Greenfield, L.G., 2009. Isotopic evidence for the provenance and turnover of organic carbon by soil microorganisms in the Antarctic dry valleys. Environ. Microbiol. 11, 597–608.

Lockheart, M.J., Van Bergen, P.F., Evershed, R.P., 1997. Variations in the stable carbon isotope compositions of individual lipids from the leaves of modern angiosperms: implications for the study of higher land plant-derived sedimentary organic matter. Org. Geochem. 26, 137–153.

Makou, M.C., Hughen, K.A., Xu, L., Sylva, S.P., Eglinton, T.I., 2007. Isotopic records of tropical vegetation and climate change from terrestrial vascular plant biomarkers preserved in Cariaco Basin sediments. Org. Geochem. 38, 1680–1691.

Matsumoto, G.I., 2008. Organic geochemical studies in the McMurdo Dry Valleys, Antarctica. Res. Org. Geochem. 23/24, 53–71 (in Japanese with English abstract).

Matsumoto, G., Torii, T., Hanya, T., 1979. Distribution of organic constituents in lake waters and sediments of the McMurdo Sound region in the Antarctic. Spec. Issue. Mem. Natl Inst. Polar Res. 13, 103–120.

Matsumoto, G., Torii, T., Hanya, T., 1981. High abundance of long-chain normal alkanoic acids in Antarctic soil. Nature 290, 688–690.

Matsumoto, G.I., Watanuki, K., Torii, T., 1988. Hydroxy acids in Antarctic lake sediments and their geochemical significance. Org. Geochem. 13, 785–790.

Matsumoto, G.I., Akiyama, M., Watanuki, K., Torii, T., 1990a. Unusual distributions of long-chain n-alkanes and n-alkenes in Antarctic soil. Org. Geochem. 15, 403–412.

Matsumoto, G.I., Hirai, A., Hirota, K., Watanuki, K., 1990b. Organic geochemistry of the McMurdo Dry Valleys soil, Antarctica. Org. Geochem. 16, 781–791.

Matsumoto, G.I., Friedmann, E.I., Watanuki, K., Ocampo-Friedmann, R., 1992. Novel long-chain anteiso-alkanes and anteiso-alkanoic acids in Antarctic rocks colonized by living and fossil cryptoendolithic microorganisms. J. Chromatogr. 598, 267–276.

Matsumoto, G.I., Fujimura, C., Minoura, K., Takamatsu, N., Takemura, T., Hayashi, S., Shichi, K., Kawai, T., 2003. Estimation of paleoenvironmental changes in the Eurasian continental interior during the last 12 million years derived from organic components in sediment cores (BDP96&98) from Lake Baikal. In: Kashiwaya, K. (Ed.), Long Continental Records from Lake Baikal. Springer-Verlag, Tokyo, pp. 75–94.

Matsumoto, G.I., Nienow, J.A., Friedmann, E.I., Sekiya, E., Ocampo-Friedmann, R., 2004. Biogeochemical features of lipids in endolithic microbial communities in the Ross desert (McMurdo Dry Valleys), Antarctica. Cell. Mol. Biol. 50, 591–604.

Matsumoto, G., Kanda, H., 1985. Hydrocarbons, sterols and hydroxyl acids in Antarctic mosses. Antarct. Rec. 87, 23–31.

Matsumoto, G.I., Watanuki, K., 1992. Geochemical features of organic components in extremely acid crater lake (Yugama) of Kusatsu-Shirane Volcano in Japan. Geochem. J. 26, 117–136.

McKelvey, B.C., Webb, P.N., 1962. Geological investigations in southern Victoria land, Antarctica. New Zealand J. Geol. Geophys. 5, 143–162.

McKinney, D.E., Bortiatynski, J.M., Carson, D.M., Clifford, D.J., De Leeuw, J.W., Hatcher, P.G., 1996. Tetramethylammonium hydroxide (TMAH) thermochemolysis of the aliphatic biopolymer cutan: insights into the chemical structure. Org. Geochem. 24, 641–650.

Naraoka, H., 2004. Isotopic composition of organic molecules. In: Ishiwatari, R., Yamamoto, M. (Eds.), Organic Geochemistry. Geochemistry Series, vol. 4. Kyouritsu Shuppan, Tokyo, pp. 201–231 (in Japanese).

O'Leary, W.M., 1982. Lipoidal contents of specific microorganisms. In: Laskin, A.I., Lechevalier, H.A. (Eds.), CRC Handbook of Microbiology). Microbial Composition: Carbohydrates, Lipids, and Minerals, 2nd ed., vol. IV. CRC Press, Boca Raton, FL, pp. 391–434.

Prebble, J.G., Raine, J.I., Barrett, P.J., Hannah, M.J., 2006. Vegetation and climate from two Oligocene glacioeustatic sedimentary cycles (31 and 24 Ma) cored by the Cape Roberts project, Victoria land basin, Antarctica. Palaeogeogr. Palaeoclim. Palaeoecol. 231, 41–57.

Reddy, G.S.N., Aggarwal, R.K., Matsumoto, G.I., Shivaji, S., 2000. *Arthrobacter flavus* sp. nov., a psychrophilic bacterium isolated from a pond in McMurdo Dry Valley, Antarctica. Int. J. Sys. Evol. Microbiol. 50, 1553–1561.

Reddy, G.S.N., Prakash, J.S.S., Prabahar, V., Matsumoto, G.I., Stackebrandt, E., Shivaji, S., 2003a. *Kocuria polaris* sp. nov., an orange-pigmented psychrophilic bacterium isolated from an Antarctic cyanobacterial mat sample. Int. J. Sys. Evol. Microbiol. 53, 183–187.

Reddy, G.S.N., Prakash, J.S.S., Srinivas, R., Matsumoto, G.I., Shivaji, S., 2003b. *Leifsonia rubra* sp. nov. and *Leifsonia aurea* sp. nov., psychrophiles from a pond in Antarctica. Int. J. Syst. Evol. Microbiol. 53, 977–984.

Thorn, V.C., 2001. Oligocene and early Miocene phytoliths from CRP-2/2A and CRP-3, Victoria land basin, Antarctica. Terra. Antarct. 8, 407–422.

Torii, T., Yamagata, N., 1981. Limnological studies of saline lakes in the dry valleys. In: McGinnis, L.D. (Ed.), Dry valley drilling project. Antarct. Res. Ser, vol. 33. Amer. Geophys. Union, Washington, D.C., pp. 141–159.

Wada, E., Shibata, R., Torii, T., 1981. ^{15}N abundance in Antarctica: origin of soil nitrogen and ecological implications. Nature 292, 327–329.

Warny, S., Askin, R.A., Hannah, M.J., Mohr, B.A.R., Raine, J.I., Harwood, D.M., Florindo, F. and the SMS Science Team, 2009. Palynomorphs from a sediment core reveal a sudden remarkably warm Antarctica during the middle Miocene. Geology 37, 955–958.

Yoshioka, T., 2006. Behavior of stable isotopes in biosphere. In: Minagawa, M., Yoshioka, T. (Eds.), Biogeochemistry. Baifukan, Tokyo, pp. 93–143 (in Japanese).

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